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*New Technique for Quantitative SiO₂ Determinations
of Silicate Materials by X-Ray Diffraction
Analysis of Glass*

Douglas B. Nash

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

July 25, 1963

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*New Technique for Quantitative SiO₂ Determinations
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ABSTRACT

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Results of an experimental X-ray study on 96 synthetic glasses show that the 2θ positions of glass diffraction maxima have an inverse relation to SiO_2 concentration in silicate glasses. This relationship is the basis of a new technique for semiquantitative determinations of SiO_2 in silicate materials by X-ray diffraction methods. Samples to be examined are fused and the resulting glass scanned from 12 to 40 deg 2θ using $\text{CuK}\alpha$ radiation. The mean 2θ position of the diffraction maximum is a measure of the SiO_2 content of the glass. Calibration curves for both weight and molecular percent SiO_2 vs 2θ are presented in this Report. The technique requires only small, unweighed amounts of sample for analysis; it is simple, rapid, and utilizes standard diffraction equipment without modification. Its accuracy, at present, allows SiO_2 determinations to within ± 1 to 4% of the actual concentration.

Arthur

I. INTRODUCTION

The study of glass with X-ray diffraction methods has been largely confined to structural investigations which attempt to explain the existence of diffraction "halos" or "maxima" on powder photographs and diffractograms, respectively. The apparent lack of compositional studies of glass with diffraction techniques is probably due to the rather "dull" nature of glass diffraction patterns. Virtually no X-ray diffraction studies have been made on natural rock glasses and fused natural rocks. In January 1963, it was noticed, during the course of diffraction studies conducted in support of one of the lunar exploration programs at the Jet Propulsion Laboratory, that the composition of glass seemed to affect the characteristics of the glass diffraction pattern. Fur-

ther investigation suggested that the 2θ position, the intensity, and the symmetry of glass diffraction *maxima* vary systematically with change in SiO_2 content of the glass (Ref. 1).

This Report presents the results of a detailed investigation of the diffraction properties of 96 silicate glass specimens of varying composition. The results confirm the earlier conclusion that angular position of the diffraction maximum of glass is a function of silica content of the glass and that semiquantitative SiO_2 determinations of rocks and other silicate materials can be made with standard diffraction equipment.

II. EXPERIMENTAL METHOD

A. Selection of Rock Samples

The intent of this study was to investigate the effects that changing SiO_2 content had on glass diffraction patterns. As a preliminary step, a number of natural glass specimens—pumice, obsidian, and tektite—were analyzed and their diffraction patterns compared with patterns from synthetic glasses made from rocks with equivalent silica content. The patterns in each case were identical, suggesting that only the SiO_2 content controlled the pattern configuration and not the history or origin of the glass. Thus it was decided to synthesize glasses of various composition by fusing natural rock specimens of varying SiO_2 content, specimens upon which complete chemical analyses had already been performed. The rocks used are of igneous origin, some being intrusive (plutonic) and some extrusive (volcanic). They come from such various parts of the world as California, Washington, Alaska, and Japan. In most cases they are crystalline in nature; however, some of the more acidic¹ volcanic rocks contain considerable glass. They range in SiO_2 content from 36 to 78 wt % (see Table 1).

Rarely do natural igneous rocks have greater than 78% silica; thus it was decided to extend the range of composition of starting materials to 100% by mixing required amounts of quartz (pure SiO_2) with a rock-base sample and therefore obtaining the desired bulk silica content. Likewise, natural igneous silicate rocks rarely have less than 36% SiO_2 ; however, no attempts were made to extend the range of samples to silica values of less than 36%.

The original chemical analyses of the rock samples were performed by several different analysts at different times over a span of 20 years. Therefore, the degree of accuracy from one sample to another is uncertain. However, many of the samples are known to have excellent, reliable analyses; using these as control points, it was concluded that the majority of the analyses are reliable.

No corrections were made to the analyses for loss of water during fusing, and they therefore represent the composition of the original rock material.

B. Glass Preparation

Most of the rock samples were obtained in powdered form, being separates of materials used in previous ana-

¹Rocks with greater than 66% SiO_2 .

lytical studies. Others were solid pieces which were crushed and split according to standard techniques. Two to 4 grams of the rock were ground to minus 60 mesh with a plattner steel mortar, then ground to minus 150 mesh in a porcelain mortar.

The minus 150 mesh powders were then fused, about 1/10 to 2 grams at a time, depending on the fusion method. Several fusion methods were tried, as shown in Fig. 1: a, electric arc, using carbon crucibles; b, oxy-acetylene torch, with carbon crucibles; and c, resistance furnace with molybdenum-foil crucibles in an inert atmosphere. The resistance furnace technique proved to be superior because it was rapid, clean, had good temperature control, was capable of temperatures up to 2000°C, allowed single fusions of relatively large amounts of rock powder, and was easily quenched. A strip of 0.002-in. molybdenum foil approximately 1/2-in. wide was slightly flexed into a shallow spoon-shape and placed between the water-cooled carbon electrodes of the furnace. About 2 grams of the rock powder was placed on the molybdenum strip and covered by a pyrex bell-jar, as shown in Fig. 1c. The jar was then purged of air with either tank nitrogen or argon. The temperature was raised slowly up to about 500°C to avoid rapid outgassing and splashing of the powder. Power requirements for fusing most rocks were approximately 7 amp at 110-v input; for rocks of very high silica content slightly more power was necessary. Once melting began, between 1100 (low silica) and 1710°C (quartz), the temperature of the element was further raised and held until the sample was visibly completely molten and convecting. The quenching process consisted of quickly reducing the current to the furnace, removing the bell-jar, and directing an air blast at the molten material, which would then solidify almost instantaneously. Total time required for fusing and quenching a single 2-gram sample was about 1 min.

The glass was then removed from the molybdenum strip by simply peeling or scraping the strip from the back of the glass puddle. The glass was reduced to fine powder (approximately 350 to 400 mesh) by grinding first in a small porcelain mortar, and finally, in an agate mortar.

C. X-Ray Specimen Mounts

Two standard sample mounting techniques were used: the dry pack, in an aluminum holder, and the acetone

Table 1. List of rock samples from which glass specimens were synthesized.
(See Fig. 11 for concentration of constituents other than SiO₂)

Sample number	Wt % SiO ₂	Rock type	Sample number	Wt % SiO ₂	Rock type
1	100.00	quartz	43	36.75	nepheline melilite basalt
2	51.30	leuconorite	44	57.25	olivine andesite
3	51.30	leucogabbro	45	65.69	olivine dacite
4	50.90	San Marcos gabbro	46	56.09	olivine basalt
5	62.9	keratophyre	47	45.13	nepheline basanite
6	52.20	gabbro	48	46.90	andesite
7	52.92	dolerite	49	51.94	melabasalt
8	63.0	basic quartz monzonite	50	50.97	hypersthene basalt
9	48.28	basalt porphyry	51	49.62	melabasalt porphyry
10	54.14	andesite	52	38.57	nepheline basalt
11	50.59	melabasalt porphyry	53	60.02	andesite
12	72.95	rhyolite obsidian	54	51.20	melabasalt (altered)
13	72.75	pumice ejecta	55	54.70	ophitic basalt
14	43.94	nepheline basanite	56	73.44	rhyolite (Mt. Lassen)
15	73.15	obsidian	57	47.78	andesite
16	70.65	Town Mountain granite	58	76.30	pumice (Mt. Katmai)
17	76.53	rhyolite obsidian	59	73.30	rhyolite obsidian
18	36.72	nepheline melilite basalt	60	69.44	volcanic (Mt. Lassen)
19	58.44	olivine andesite	61	48.74	basalt porphyry
20	65.58	pyroxene rhyodacite	62	53.36	volcanic (Mt. Katmai)
21	71.33	rhyolite	63	67.04	biotite-hornblende dacite
22	65.58	pyroxene dacite	64	48.50	subophitic basalt
23	72.40	rhyolite glass	65	73.10	pumice
24	64.52	pumice	66	72.98	biotite rhyolite pumice
25	72.22	rhyolite tuff	(The following samples were synthesized by mixing quartz with portions of several of the above-listed rocks)		
26	69.00	granodiorite	600	98	quartz + sample 58
27	56.98	augite andesite	601	96	↓
28	58.90	quartz diorite	602	94	
29	77.96	pumice	603	92	
30	37.10	nepheline basalt	604	90	
31	66.24	hypersthene dacite	605	88	
32	66.03	pumice	606	86	quartz + sample 24
33	67.33	pumice	607	84	↓
34	63.52	pumice	608	82	
35	58.70	basaltic andesite	609	80	
36	73.60	dacite	610	76	
37	52.30	diabase	611	75	
38	50.08	melabasalt	612	74	↓
39	42.30	picrite basalt	613	64	
40	65.70	dacite	614	63	
41	37.22	nepheline melilite basalt	615	62	
42	47.64	andesite			↓

Table 1 (Cont'd)

Sample number	Wt % SiO ₂	Rock type	Sample number	Wt % SiO ₂	Rock type
616	61	quartz + sample 54 *	623	41	quartz + sample 43
617	60	quartz + sample 54	624	40	↓
618	47	quartz + sample 52	625	39	
619	46	↓	626	38	
620	44		627	45	quartz + sample 52
621	43	quartz + sample 30	628	58	quartz + sample 44
622	42	quartz + sample 43	629	83.6	quartz + sample 24

smear, on glass microscope slides (Fig. 2). It would seem that the pack technique is obviously preferable because it avoids the possibility of the X-rays "seeing through" the sample into the glass mounting plate and "contaminating" the diffraction pattern. However, comparison of patterns obtained from the same specimen mounted in each of the above fashions showed that no deleterious effects were caused by the glass slide mount. Therefore, to avoid the necessity of making relatively large amounts of glass and to expedite mounting of the 96 samples, the glass-smear technique was utilized for the majority of the samples, while checks were run with pack-mounted specimens on several samples throughout the compositional range to ensure that the data were not being significantly affected by mounting procedures.

The smear mounts were made by transferring a small amount of the finely ground glass specimen from the agate mortar onto a standard 1-11/16 × 1-in. microscope slide, adding a drop or two of acetone, and smearing the mixture uniformly over the surface of the slide. No binding agent was used. The pack mounts were made by pressing the glass powder into a standard Norelco aluminum sample holder, backed with a microscope coverglass and adhesive tape.

D. X-Ray Analysis and Instrument Parameters

In contrast to the many sharp diffraction peaks from crystalline material, glasses produce only a single broad peak on a strip-chart recording. This peak will be referred to as the "diffraction maximum" or simply "maximum." The maximum corresponds in origin to the so-called diffraction ring or halo that occurs on powder photographs of glass materials. (No film work was done during the course of this study.) A typical glass diffraction spectrum is compared with its crystalline equivalent

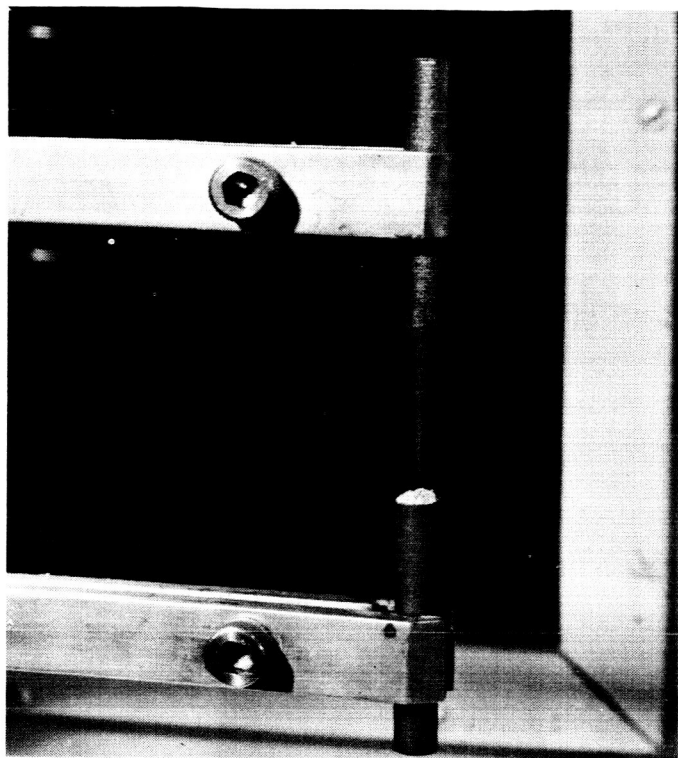
in Fig. 3; note the broad maximum which occurs between 12 and 40 deg 2 θ on the glass pattern.

Diffraction spectra for each glass specimen were obtained on a standard Norelco diffraction unit with counter goniometer, pulse-height analyzer (PHA), and strip-chart recorder. Preliminary evaluation of X-ray tube and counter types indicated that copper radiation and a side-window proportional counter were most efficient in producing and detecting the glass-diffraction spectrum. It was found that iron radiation produced no diffraction maximum at all.

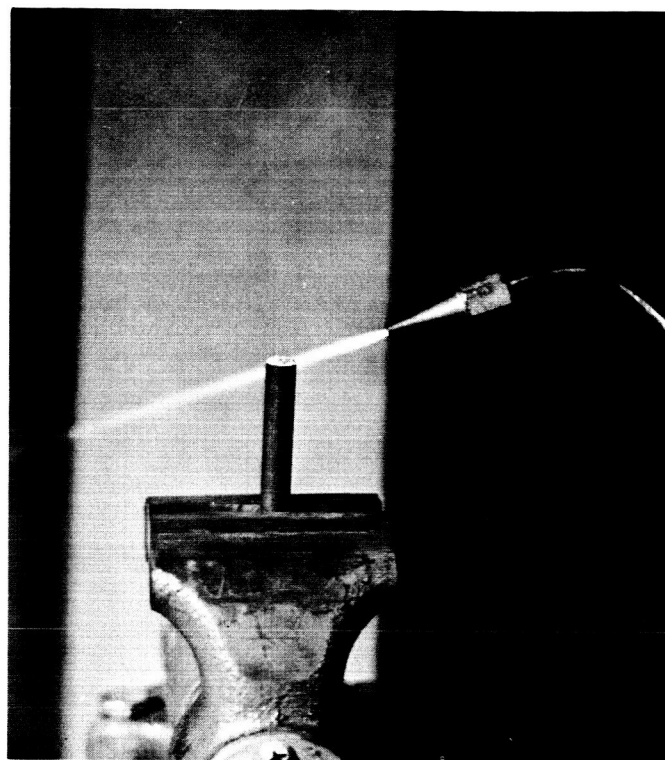
Experiments were conducted to determine what instrument parameters produced optimum resolution of the glass maxima. For example, it was found that by increasing the beam current and voltage the maximum for obsidian was greatly increased in intensity, as shown in Fig. 4. Various scan rates, time constants, and slit sizes were also tried, with results as shown in Fig. 5. The parameters finally decided upon are listed in Table 2. These were used for all of the 96 specimens examined, with the exception that in some cases, due to the use of two different diffraction units that had slightly different intensity characteristics, the beam voltage was reduced on one unit to 45 kv instead of 50 kv in order to prevent the recorder pen from going off scale. A baseline on the PHA was chosen (separate settings for each unit) to discriminate partially against fluorescent FeK α radiation which was produced in low-silica, high-iron samples (see Section IV).

E. Measuring 2 θ Position and Intensity of Maximum

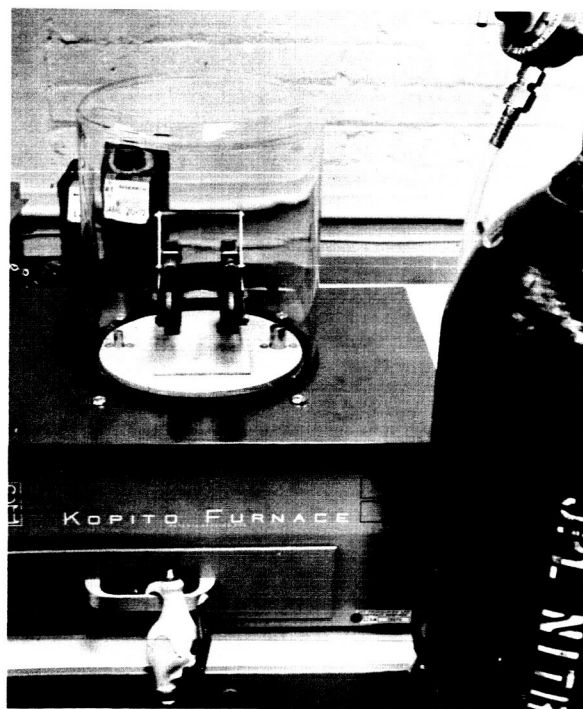
Each glass specimen was scanned three times between 12 and 40 deg 2 θ . Several characteristics of the resulting



a. Electric arc, with carbon crucible



b. Oxyacetylene torch, with carbon crucible



c. Resistance furnace with molybdenum-foil element and nitrogen atmosphere

Fig. 1. Various fusion methods tried for glass synthesis



Fig. 2. X-ray mounts of glass specimens, and apparatus used in preparation of mounts.
Pack mount on left, acetone smear on right

maxima were measured and averaged over the three runs, the most important being the 2θ position. The very first method of measurement tried proved to be most reproducible as well as simplest. It consisted of drawing a best-fitting straight line through and parallel to each

slope of the maximum as shown diagrammatically in Fig. 6. The maximum position then was defined by the 2θ position of the intersection of the two lines. Admittedly, this technique lends itself to some subjectivity, since various individuals would draw the lines in slightly different positions. However, the amount of possible variation is relatively small as long as the maximum has been adequately resolved by the diffractometer. For example, compare Fig. 5a and 5d; it is obvious that the position of lines drawn through the upper portion of the slopes of Fig. 5d are more reproducible than similar lines through 5a.

Several other methods of measuring the maximum position were tried, such as center-of-gravity determinations and the use of an "average curve" template (Fig. 7), but all proved to be less reproducible, no less subjective, and produced no less dispersion in the resulting data. The straight-line method, however, leaves much to be desired, and it is possible that a better technique can be developed in the future.

The intensity of the maxima was measured as the mean highest level of the crest of the maximum curves, and the background intensity was arbitrarily measured at the break in slope of the high (2θ) portion of the maximum curve (Fig. 6).

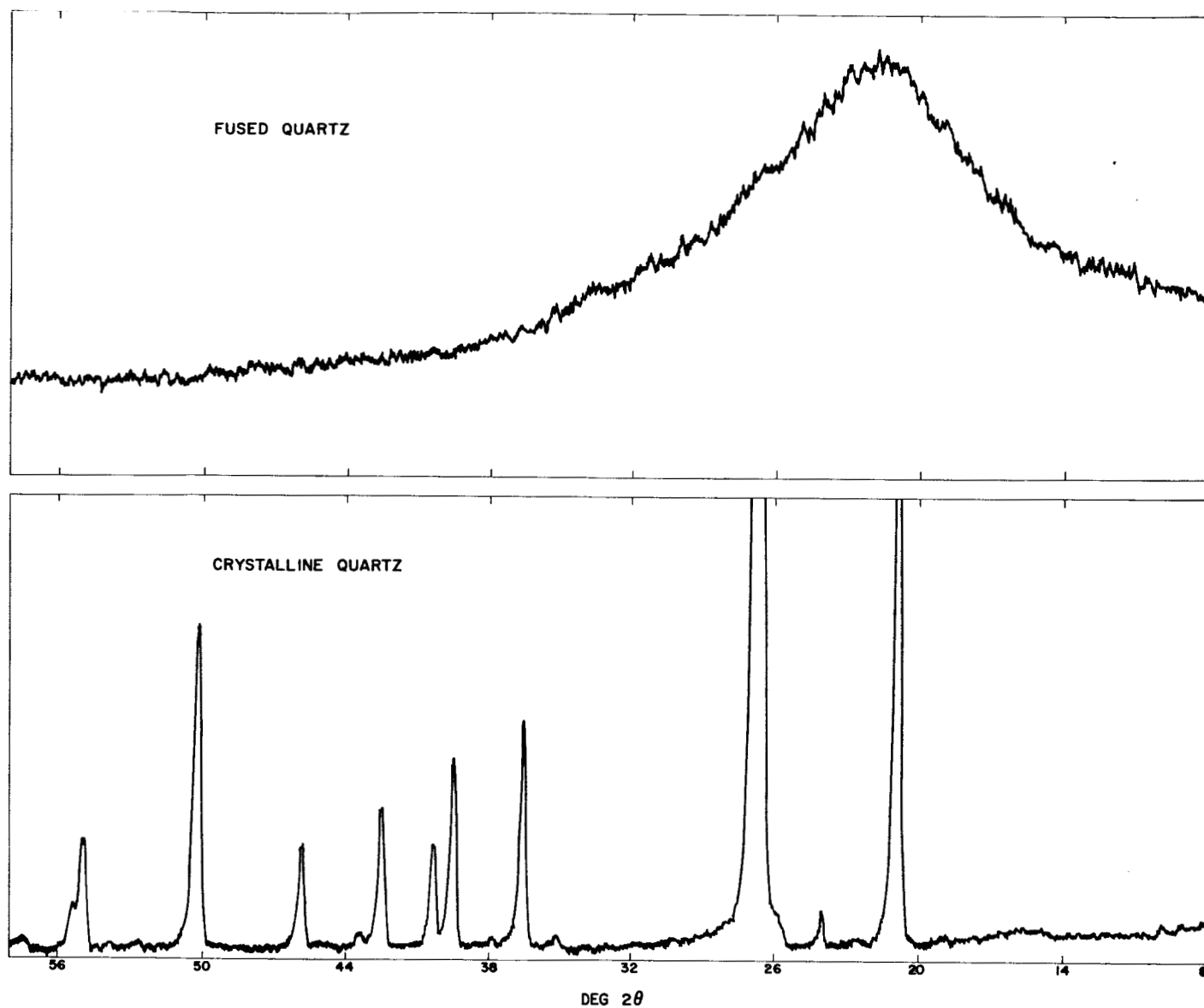


Fig. 3. Comparison of X-ray diffraction spectra obtained from fused quartz (top) and crystalline quartz (bottom). Instrument parameters were: $\text{CuK}\alpha$ radiation, 50 kv, 25 ma (glass), 40 kv, 10 ma (crystalline); proportional detector, 1650 v; slits 1° , 0.006 in., 1° ; scan rate, $1^\circ/\text{min}$; time constant, 8, $\times 200$

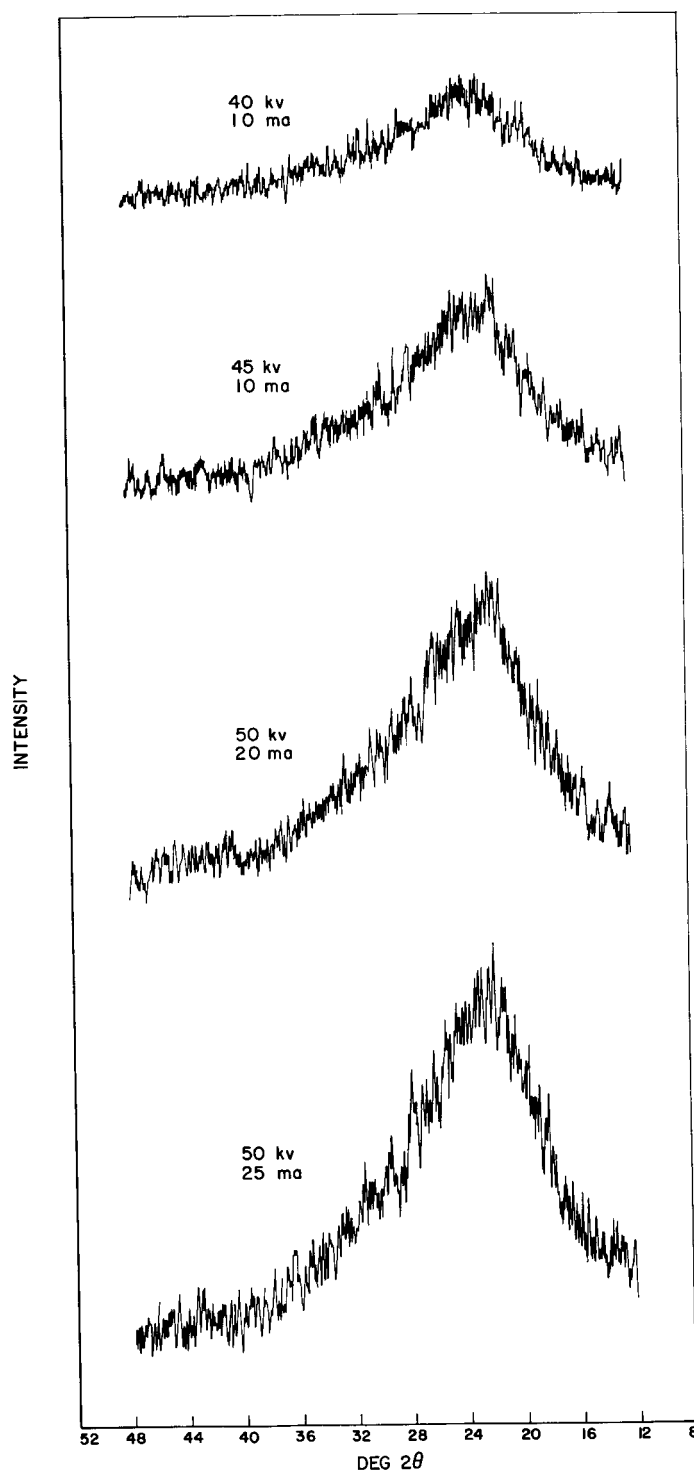


Fig. 4. Effect of increased beam voltage and current on intensity of glass diffraction maximum of natural obsidian (wt % $\text{SiO}_2 \approx 73$). $\text{CuK}\alpha$; proportional detector, 1650 v; slits 1° , 0.003 in.; 1° , scan rate, $2^\circ/\text{min}$; time constant 2, $\times 100$

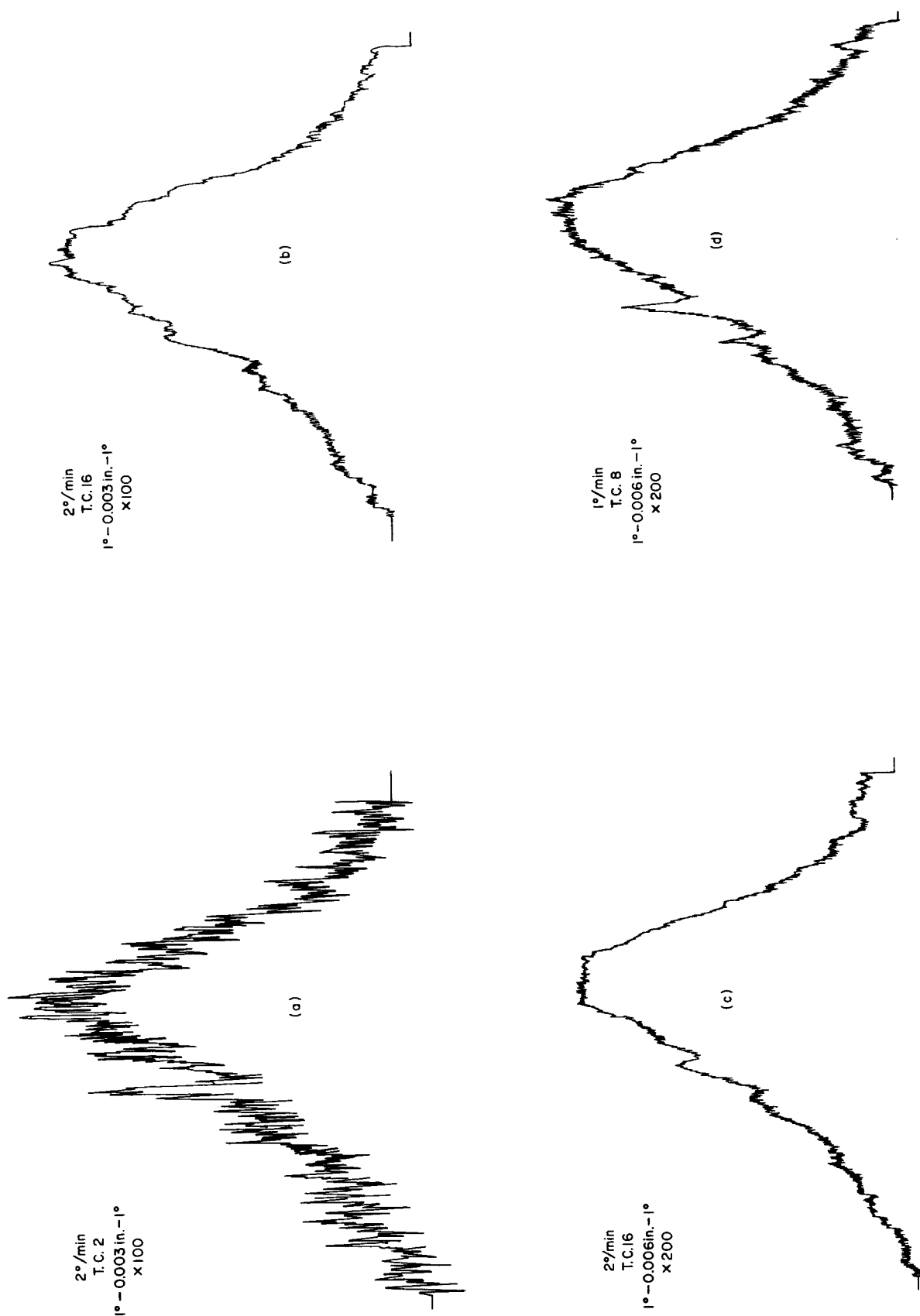


Fig. 5. Effect of various scan rates, time constants, and slit sizes on resolution of glass diffraction maxima of synthetic rock glass (wt % $\text{SiO}_2 = 73$)

Table 2. Diffractometer parameters for optimum resolution and scanning time of glass diffraction maxima

Parameter	Value
Radiation	CuK α
Beam voltage	50 kv
Beam current	25 ma
Detector	Proportional
Detector voltage	1650 v
PHA baseline	7.5 v (or as required)
Scan rate	1°/min
Time constant	8
Divergence slit	1°
Receiving slit	0.006 in.
Anti-scatter slit	1°
Scale factor	$\times 200$

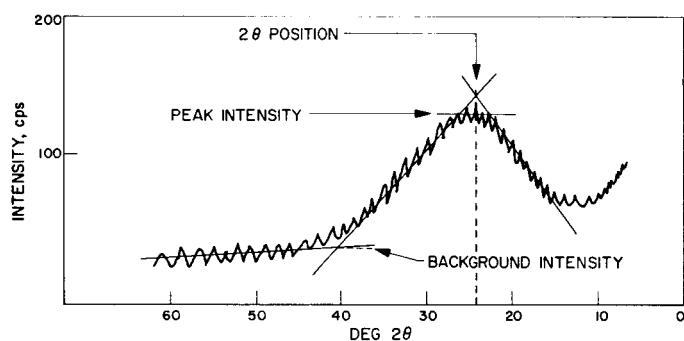


Fig. 6. Diagrammatic sketch of straight-line method of measuring 2θ position, intensity, and background level of glass diffraction maximum

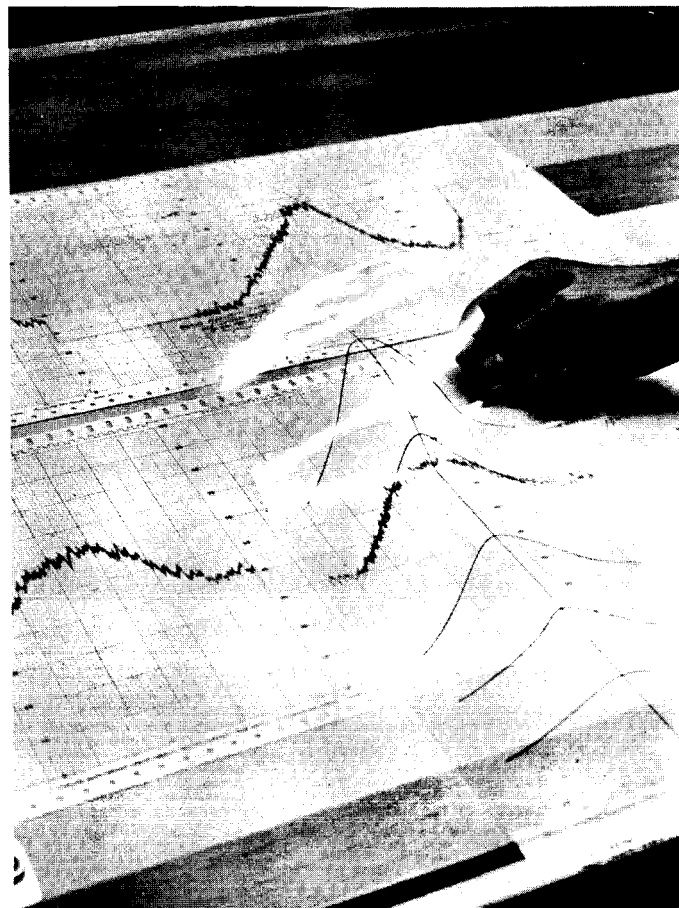


Fig. 7. Template method of determining 2θ position of glass maximum. Best-fitting "average" curve on template is matched with glass maximum. 2θ determined by position of vertical line on template. This method turned out to be more subject to errors than straight-line method

III. EXPERIMENTAL RESULTS

A. Data Plots

Results of the 96 glass diffraction analyses are listed in Table 3. The 2θ position of each maximum (average of three runs) plotted as a function of SiO_2 composition of the glass is shown graphically in Fig. 8a and 8b. The SiO_2 content has an inverse relation to the 2θ position of the glass maximum; the higher the SiO_2 content the lower the 2θ position (Fig. 9).

The 2θ values plotted as a function of concentration of other oxide components is shown in Fig. 10. It appears at first glance that there is a strong linear relation between 2θ and several of the other oxides, such as CaO , MgO , and FeO . However, this relation is intrinsic with the silica content because, as is shown in a variation diagram of oxides vs SiO_2 , Fig. 11, the concentration of other oxides in igneous rocks is not independent of silica content. Thus Fig. 10 is merely the equivalent of Fig. 11 with ordinate plotted inversely to correspond with the inverse relation between 2θ and SiO_2 .

The intensities, or peak heights, of glass maxima, as well as their background intensities, are plotted in Fig. 12. It is clear that the intensities of the maxima are also directly proportional to the SiO_2 content of the glass (Fig. 12a), though the scatter is greater than that for 2θ . The background intensity, though not related directly to SiO_2 content (Fig. 12b), is related to iron content, as shown in Fig. 12c.

B. Reproducibility

Reproducibility runs were conducted on one basalt sample which was powdered and separated into 10 parts. Each part was then fused, repowdered, and run separately in the diffractometer. The results are shown in Table 4; the maximum deviation from the mean 2θ position was about 0.50 deg. This represents uncertainties in sample splitting, grinding, fusing, regrinding, mount preparation, and instrument reproducibility.

Each of the 96 specimens was scanned three times and the average 2θ value recorded. The deviation from mean here was considerably less than that for the separate fusions, averaging ± 0.15 deg.

C. Effect of Incomplete Fusion

When the experimental 2θ data were first plotted, several points did not fit the general curve defined by

points in Fig. 8a and 8b. It was discovered that samples represented by these points had not been completely fused. The diffraction spectrum for each sample contained regular diffraction peaks from unfused crystalline phases superimposed on the glass maximum. The unfused high-temperature phases, being rich in SiO_2 , caused the resulting glass to be deficient in SiO_2 relative to the total SiO_2 of the sample, and the diffraction maximum occurred at a correspondingly higher 2θ . When the samples were re-fused, their diffraction maxima occurred at lower 2θ values, commensurate with the systematic trend.

D. Uncertainties and Probable Errors

Several sources of error, some of which have already been mentioned, contribute to uncertainty in the data relating SiO_2 content to 2θ . First, it should be emphasized that the values for SiO_2 percentage of points defining the curves in Fig. 8a and 8b are those of the original, unfused rock specimens—not of the actual glass material. Thus, the loss of volatiles during fusion is not compensated for, though it would be a simple matter to recompute the silica content on a water-free basis. But this assumes that only water is lost during fusion, when actually other constituents, e.g., alkalis, may also be partially lost.²

Another source of uncertainty is in the method of measuring the 2θ position of the maxima. With the straight-line method, as described in Fig. 6, there is a certain amount of subjectivity in choosing where to draw the lines, and the resulting 2θ 's may vary as much as 0.3 deg, depending on the resolution of the maxima. It was found that for higher silica glasses the resolution was very good, and the average deviation in measurements was as low as 0.1 deg.

Further uncertainty could be due to errors in the original chemical analyses, variations in X-ray flux, counter characteristics, recorder response, and deficiencies in sample preparation.

²At the time this document went to press, analytical data on composition change during fusion had not yet been received from foreign analyst.

Table 3. Data for 96 glass diffraction analyses. 2θ = angular position in degrees of mean diffraction maxima, I = intensity of maxima in counts/sec, B = background intensity (see Fig. 6) in counts/sec.
(For other chemical components of specimens see Fig. 11)

Sample number	Wt % SiO ₂	Mol % SiO ₂	2θ	I	B
1	100.00	100.00	21.11	175	60
600	97.98	98.69	21.44	151	53
601	95.96	97.36	21.58	154	58
602	93.94	96.01	21.93	144	56
603	91.92	94.65	21.71	148	55
604	89.90	93.26	21.56	186	70
605	87.88	91.85	21.82	156	45
606	86.00	89.12	21.76	175	77
607	84	87.50	22.05	140	53
629	83.58	87.16	21.74	188	90
608	82	85.86	22.02	176	81
609	80	84.21	22.07	174	83
29	77.96	85.39	22.36	191	58
17	76.53	82.51	22.24	148	54
58	76.30	83.33	22.21	166	67
610	76	80.84	22.34	148	60
611	75	80.00	22.32	181	90
612	74	79.14	22.43	147	56
36	73.60	—	22.30	150	63
56	73.44	81.21	22.29	167	78
59	73.30	—	22.47	163	77
15	73.15	79.30	22.64	175	80
65	73.10	79.59	22.55	176	79
66	72.98	81.71	22.64	150	56
12	72.95	—	22.51	176	80
13	72.75	79.31	22.67	153	66
23	72.40	79.12	22.71	148	59
25	72.22	80.08	22.60	149	60
21	71.33	77.51	22.62	146	60
16	70.65	77.93	23.56	165	96
60	69.44	77.53	22.78	160	76
26	69.00	76.14	22.85	136	70
33	67.33	73.80	23.07	154	72
63	67.04	73.91	22.92	155	71
31	66.24	71.21	22.95	158	73
32	66.03	73.91	23.20	153	71
40	65.70	71.55	23.30	145	66
45	65.69	69.81	23.70	159	87
20	65.58	71.51	23.27	137	63
22	70.08	77.80	22.77	147	56
24	64.52	70.80	23.02	141	62
613	64	70.38	23.49	166	86

Table 3 (Cont'd)

Sample number	Wt % SiO ₂	Mol % SiO ₂	2 θ	I	B
34	63.52	70.67	23.28	149	67
8	63.00	71.65	23.52	163	82
614	63.00	69.47	23.50	133	55
5	62.90	68.48	23.60	145	67
615	62	68.55	23.69	179	96
616	61	65.65	23.83	134	65
53	60.02	66.73	23.77	160	90
617	60.00	64.69	24.08	173	101
28	58.90	64.97	24.08	152	80
35	58.70	63.81	24.62	133	73
19	58.44	64.06	23.79	137	74
628	58.10	63.46	24.68	143	70
44	57.25	62.66	24.91	166	109
27	56.98	62.81	24.52	155	93
46	56.09	59.57	24.99	158	97
55	54.70	55.35	25.12	153	97
10	54.14	61.63	24.79	147	72
62	53.36	59.44	24.73	142	83
7	52.92	58.31	24.80	121	58
37	52.30	56.74	25.03	165	106
6	52.20	60.77	24.40	129	—
49	51.94	55.59	26.10	164	116
3	51.30	56.41	24.60	118	55
2	51.30	58.25	24.45	130	70
54	51.20	56.19	25.32	125	73
50	50.97	53.63	25.86	160	104
4	50.90	54.89	25.5	30	23
11	50.59	54.29	25.46	133	77
38	50.08	54.55	25.18	154	92
51	49.62	51.24	26.40	123	75
61	48.74	53.38	25.77	168	116
64	48.50	50.98	25.82	145	84
9	48.28	55.07	25.27	145	76
57	47.78	50.98	26.08	157	95
42	47.64	46.48	26.79	131	82
618	47	49.52	26.33	122	62
48	46.90	52.84	25.90	165	96
619	46	48.47	26.60	160	99
47	45.13	50.37	26.70	155	100
627	45	47.49	27.48	123	66
620	44	46.50	27.65	119	68
14	43.94	46.18	26.68	133	84
621	43	45.81	28.39	162	114
39	42.30	43.67	28.96	144	85

Table 3 (Cont'd)

Sample number	Wt % SiO ₂	Mol % SiO ₂	2 θ	I	B
622	42	45.24	28.73	119	75
623	41	44.24	28.27	163	110
624	40	43.21	28.38	118	68
625	39	42.14	28.82	126	78
52	38.57	40.97	28.95	146	100
626	38	41.17	29.38	122	73
41	37.22	40.03	30.02	149	106
30	37.10	39.79	30.38	134	92
43	36.75	39.87	30.30	152	109
18	36.72	39.19	30.62	129	91

Table 4. Results of reproducibility runs on synthetic basalt-glass. Ten fractions of the same rock sample were individually fused and examined in the diffractometer

Glass number	2 θ	Mean	Deviation from mean	Maximum deviation
141A-1	27.18	} (26.73)	+0.45	(+0.52 -0.53)
141A-2	27.20		+0.47	
141A-3	26.20		-0.53	
141A-4	26.25		-0.48	
141A-5	26.30		-0.43	
141A-6	26.85		+0.12	
141A-7	26.40		-0.33	
141A-8	27.25		+0.52	
141A-9	27.15		+0.42	
141A-10	26.50		-0.23	

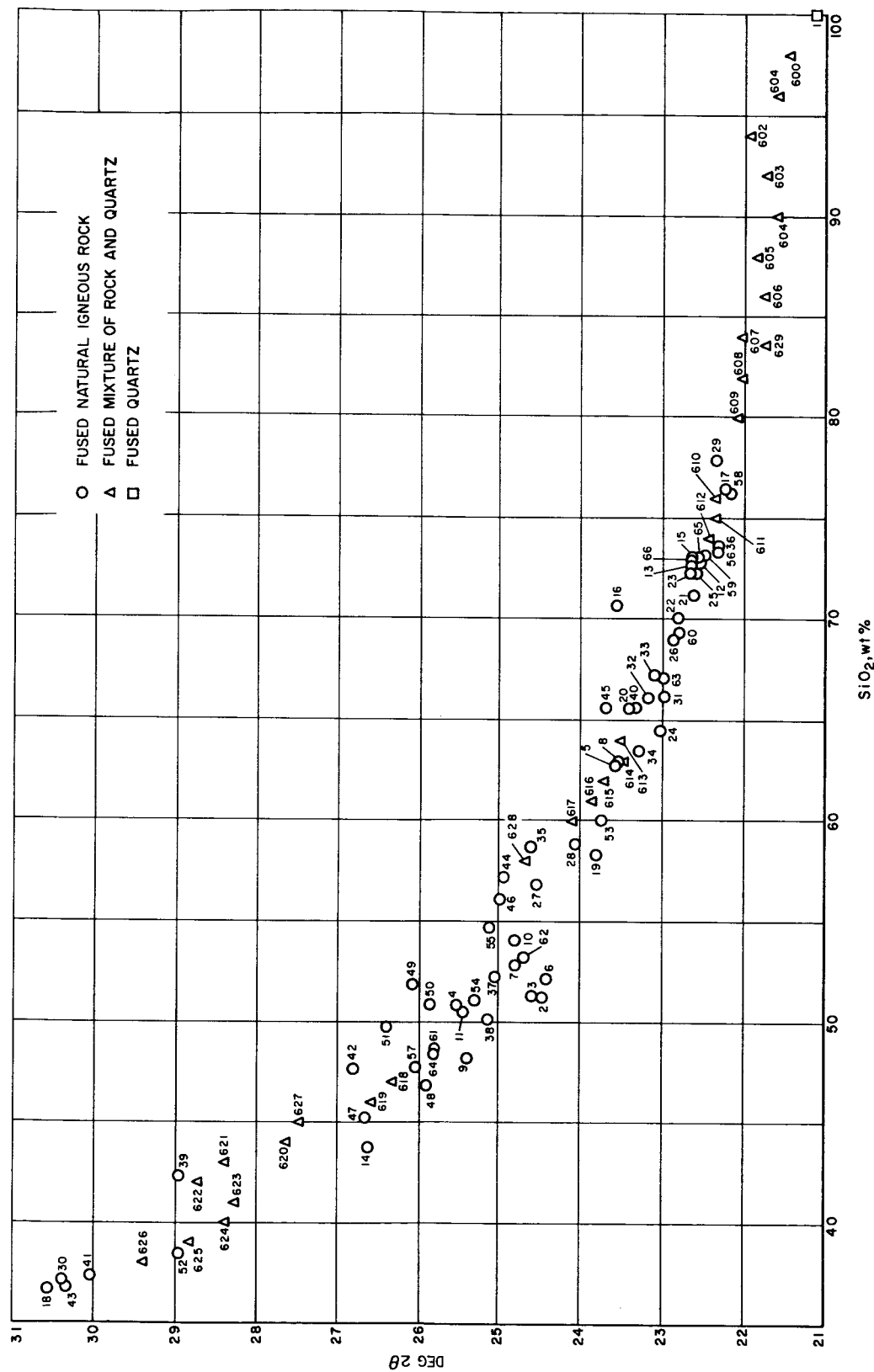
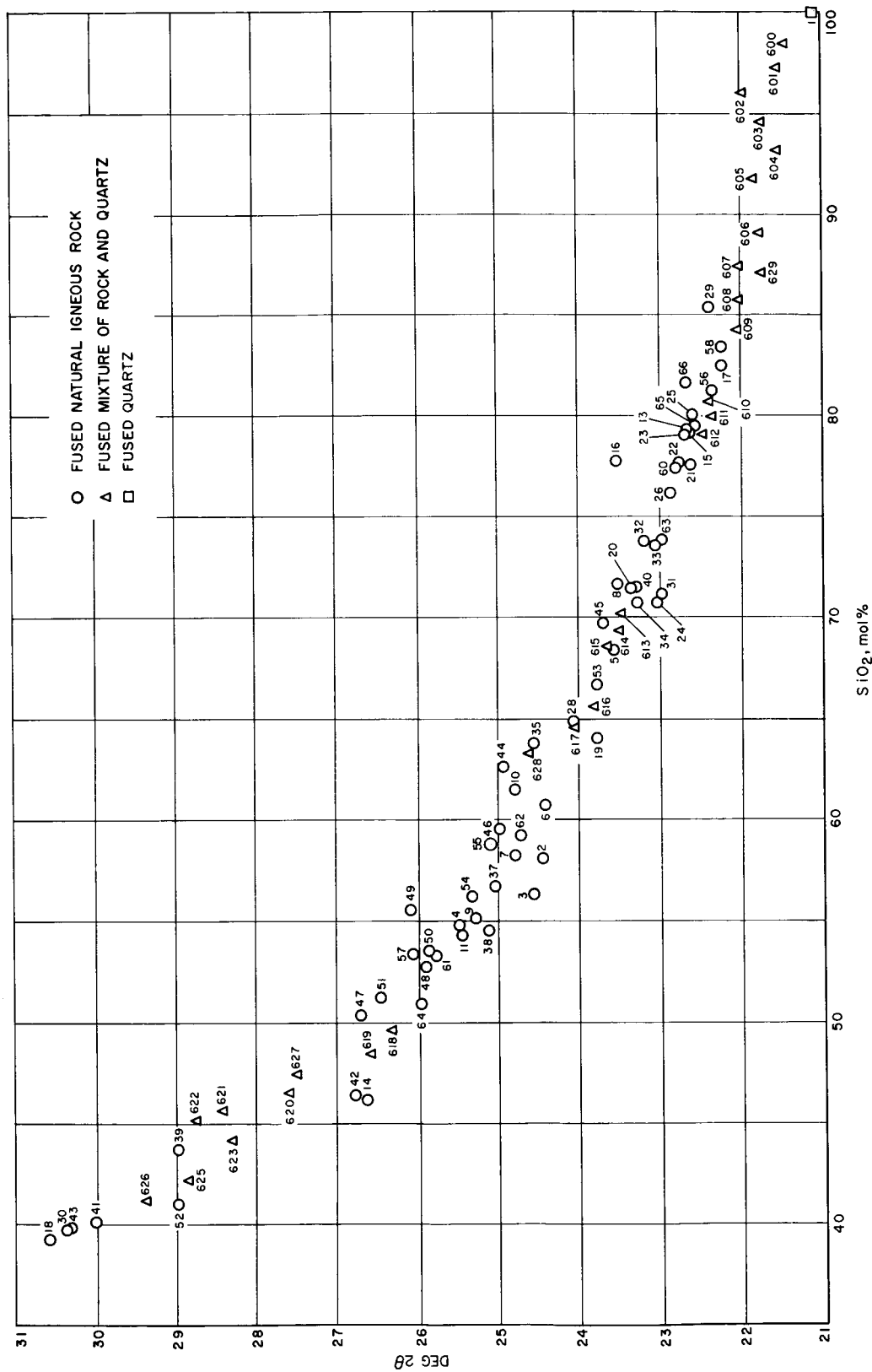


Fig. 8. 2θ position of glass diffraction maxima vs SiO₂ concentration in the glass

a. Weight percent



b. Molecular percent
Fig. 8. (Cont'd)

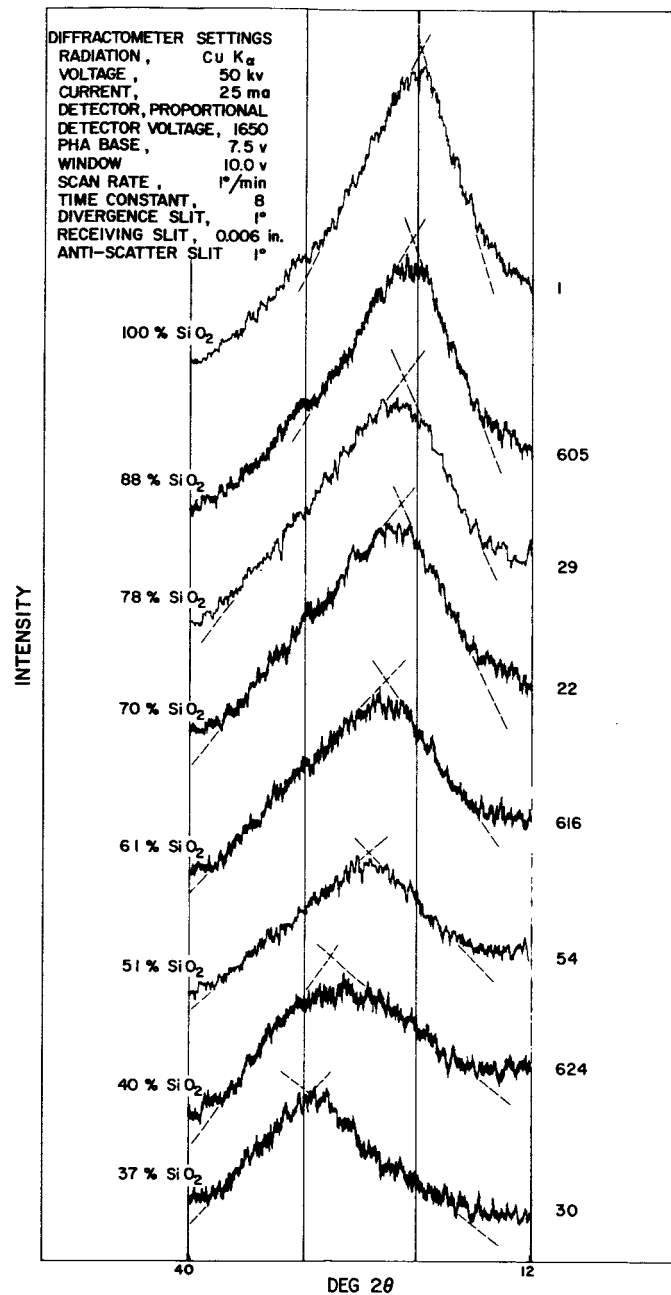


Fig. 9. Typical glass diffraction maxima for several of the 96 analyzed glass specimens, showing how maximum shifts to higher 2θ values with decreasing SiO₂ content of the glass

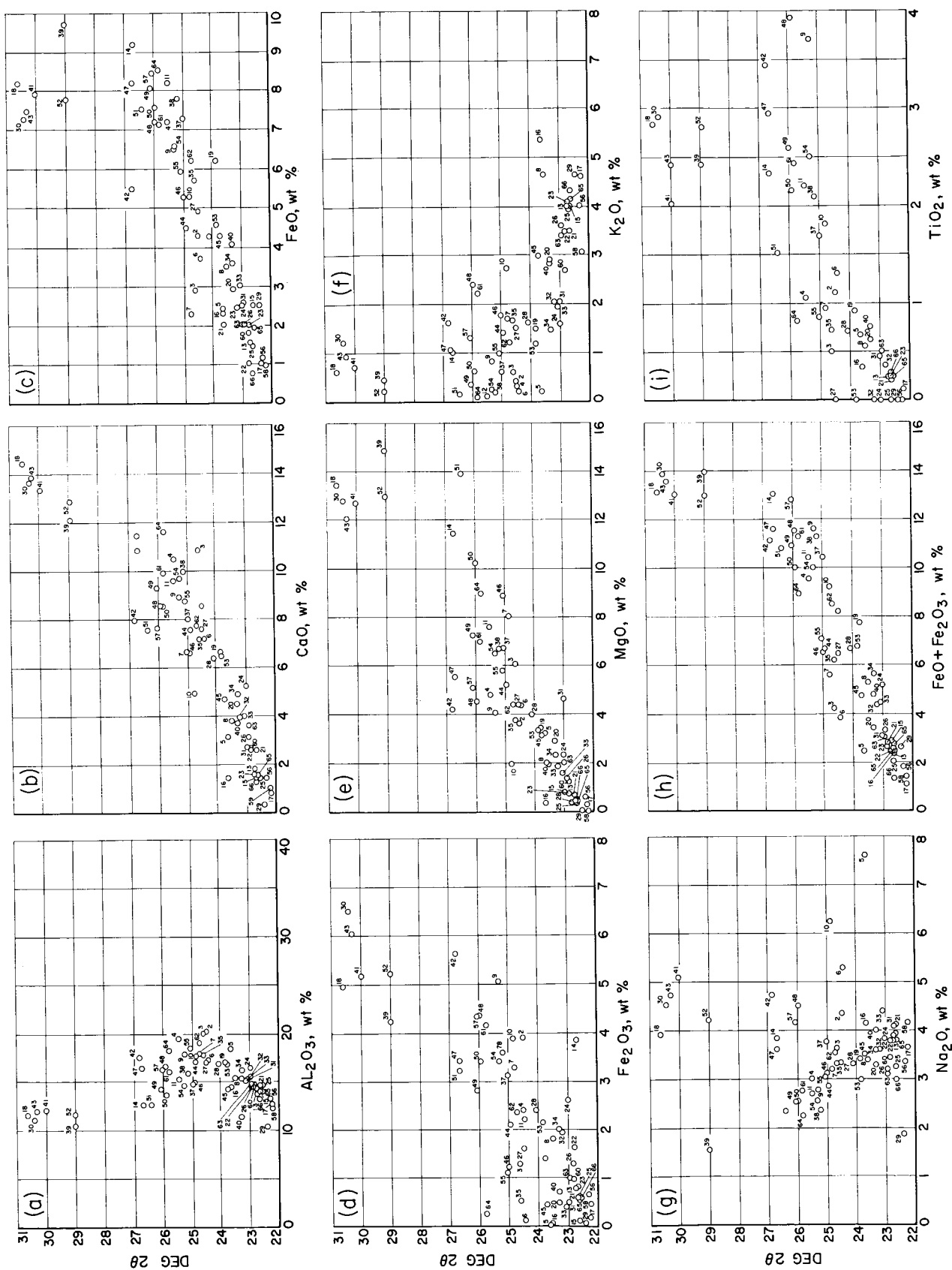


Fig. 10. 2θ position of glass diffraction maxima vs concentration of other oxide constituents of the glass.
(Compare this with Fig. 11)

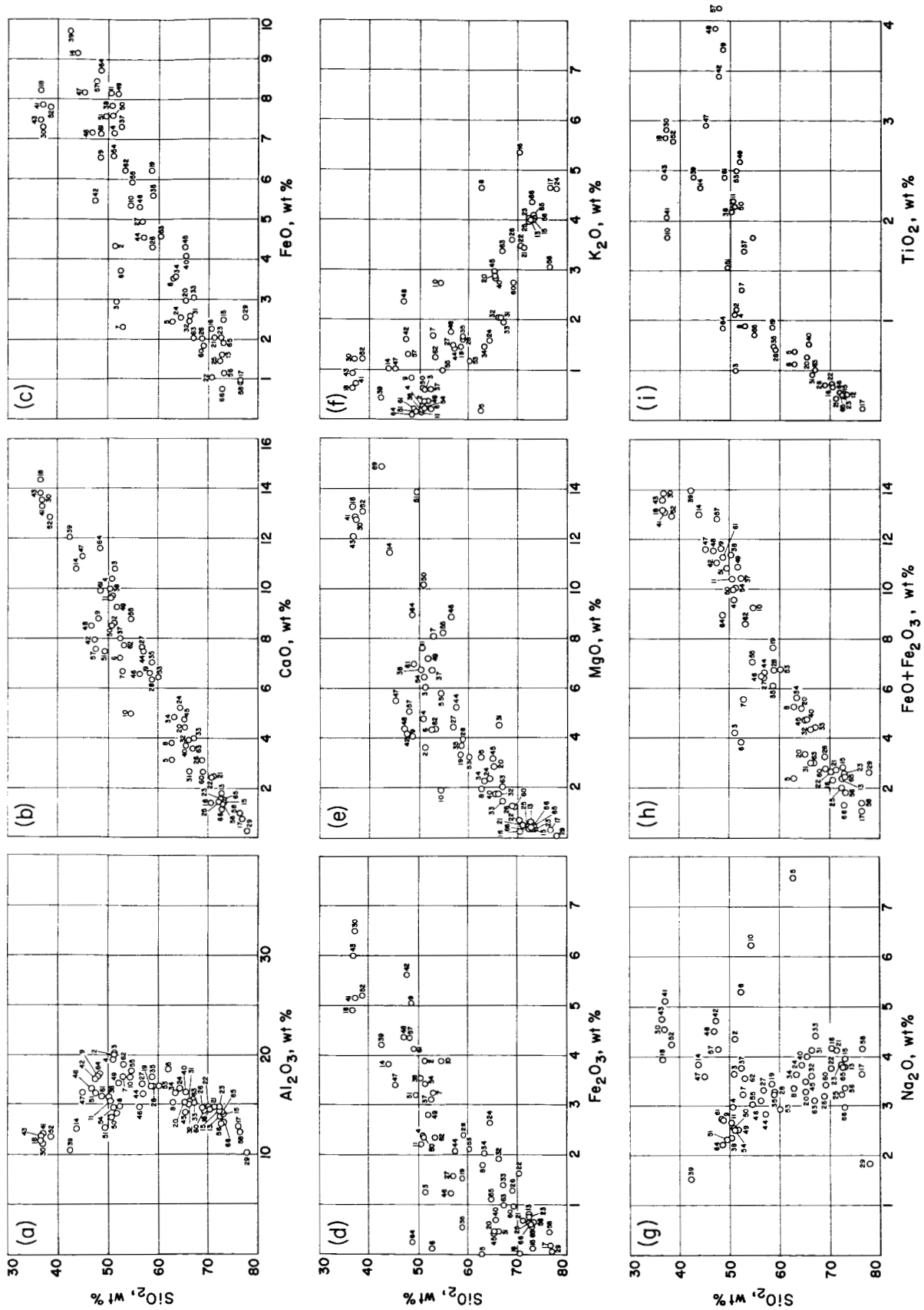
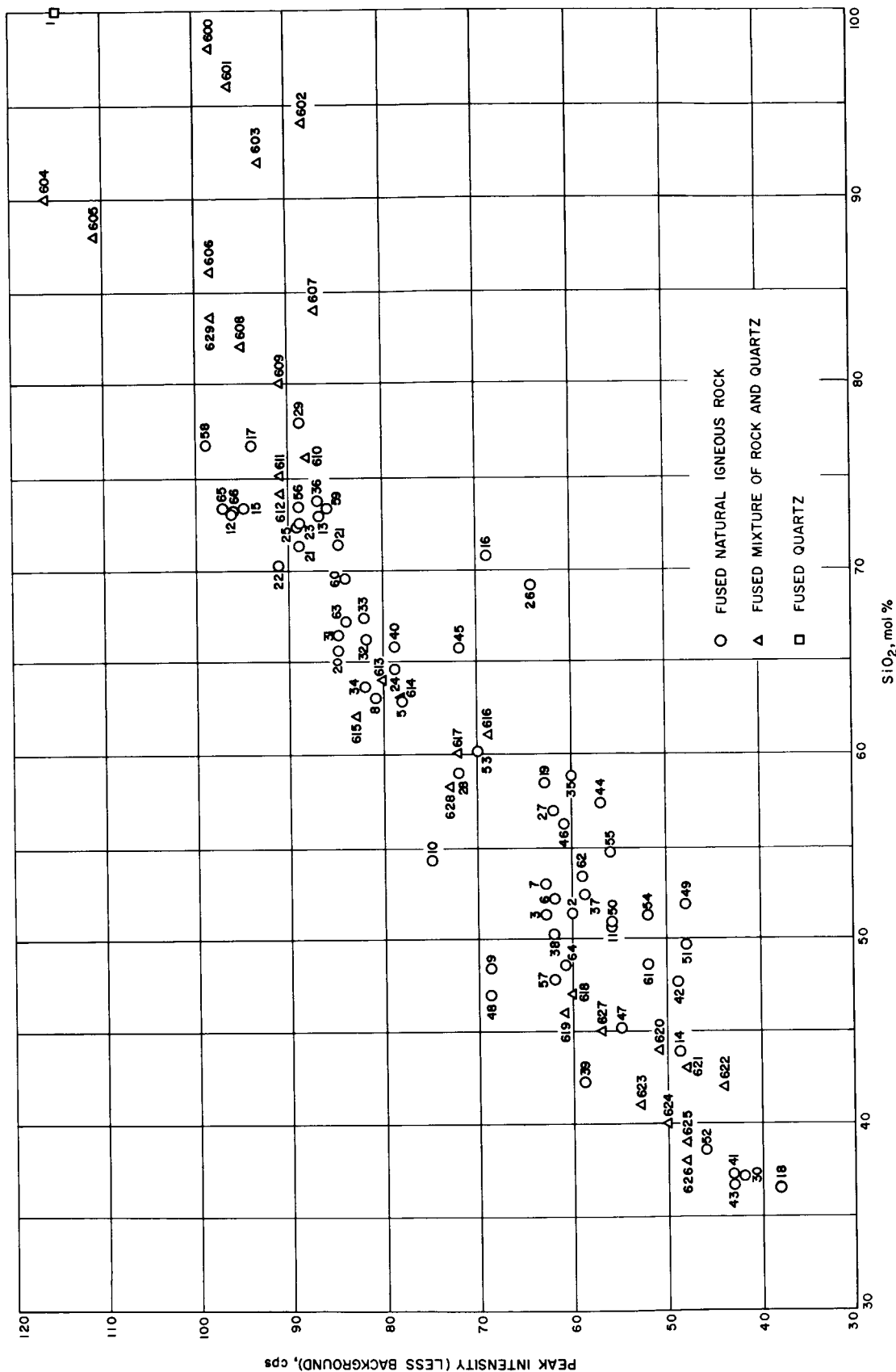
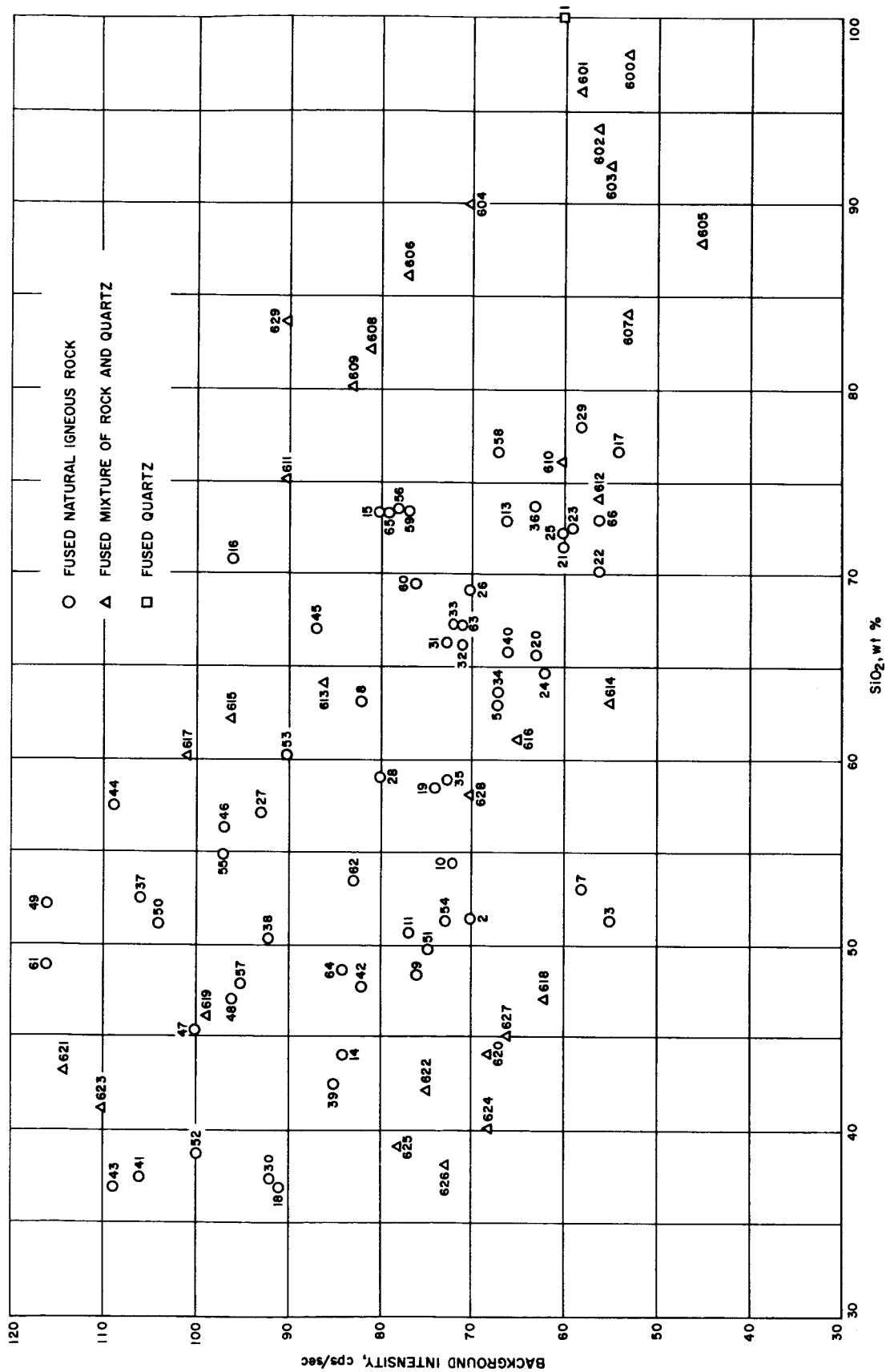


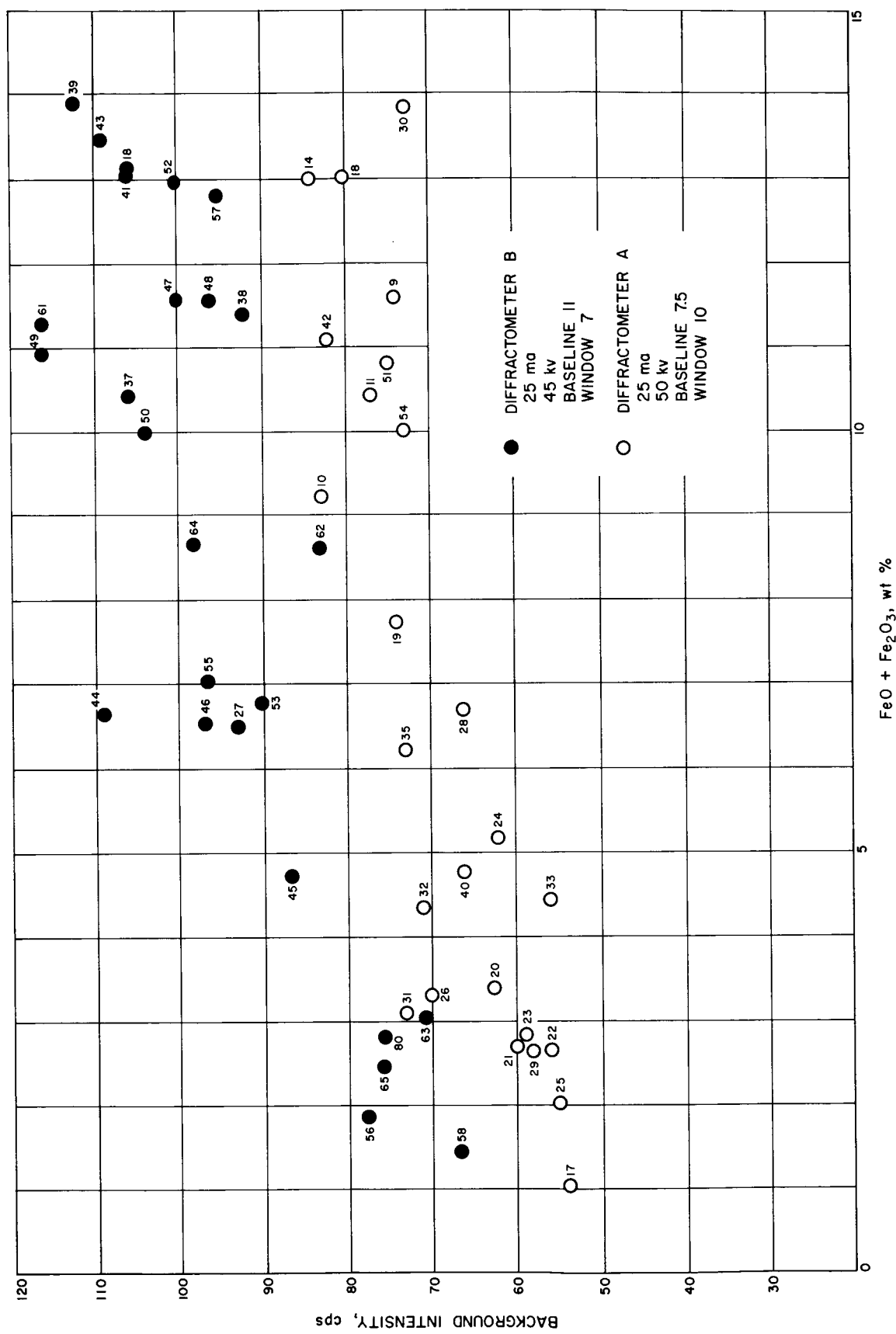
Fig. 11. Variation diagram of SiO_2 vs other oxide constituents of analyzed rocks from which glass specimens were synthesized



a. Intensity of glass diffraction maxima vs SiO₂ contents of glass
Fig. 12. Glass maxima and background intensities



b. Background intensity vs SiO_2 content
Fig. 12. (Cont'd)



c. Background intensity vs total iron content
Fig. 12 (Cont'd)

IV. DISCUSSION OF RESULTS

The data indicate that for glasses made from natural igneous rocks the SiO_2 content is the primary factor controlling the 2θ position and intensity of the glass diffraction maxima. Even though some of the other oxide components of the glasses show a systematic relationship to 2θ (Fig. 10), it is clear from comparing Fig. 10 and 11 that this relationship is an intrinsic expression of the silica relationship, since the concentration of the other oxides is dependent on SiO_2 content (for igneous rocks). Furthermore, the synthetic mixtures of rock and quartz (pure SiO_2) resulted in glasses whose diffraction maxima positions (points numbered from 600 to 629 in Fig. 8a and 8b) fell on the same curve as that for the natural igneous rock glass. This indicates that silica content alone controlled the 2θ position, since the concentration percentage of other oxides changed upon adding quartz to increase the SiO_2 content.

Earlier results (Ref. 1) based on only a small number of samples suggested that Al_2O_3 also played a role in controlling the 2θ position. It appeared then that, with a given SiO_2 concentration, a higher Al_2O_3 concentration

produced lower 2θ values. However, the present study has shown no such relationship for natural and synthetic rock glasses.

The background intensity, as defined in Fig. 6, varied directly with iron content of the glass, as shown in Fig. 12c; two sets of points are shown, each representing data obtained from separate diffraction units whose detector pulse-amplitudes, PHA settings, and resulting counting intensities were slightly different. The increase in background intensity was clearly due to increased $\text{FeK}\alpha$ fluorescence with higher total iron content ($\text{FeO} + \text{Fe}_2\text{O}_3$) of the glass.

The presence of fluorescent $\text{FeK}\alpha$ radiation and consequent high background intensity accounts also for the relatively poor resolution of low-silica glass maxima (lower curves, Fig. 9). Even though PHA discrimination of iron was attempted, it is impossible to discriminate the iron completely (because its pulse distribution overlaps that of $\text{CuK}\alpha$) without severely decreasing the $\text{CuK}\alpha$ intensity. Therefore, some of the iron pulses got through and raised the general background level.

V. THEORETICAL CONSIDERATIONS

A brief attempt will be made to review the present concepts of glass structure and suggest the relation between that structure and X-ray scattering properties observed in this study. It has been known for many years that glass and other noncrystalline substances produce only a broad maximum of X-ray scattering on diffraction patterns or powder photographs. Attempts at explaining this phenomenon have led to various theories ranging from the early concept of glass composed of sub-micron crystals, the *crystallite theory* (Ref. 2) to later *random network theory* (Ref. 3 and 4), and more recently to the idea that glass is composed of discrete building blocks called *vitrons* (Ref. 5), which reflect a semi-ordered crystalline structure.

As early as 1915, Debye and Ehrenfest (Ref. 6 and 7) proved theoretically that diffraction maxima would be produced by glass if there were interatomic distances occurring repeatedly in the structure. The so-called *radial distribution analysis* commonly used in the X-ray study of glass (for example, see Ref. 8) shows that the numerical value of these interatomic distances can be determined from observed scattering intensity. These distances in silicate glass correspond with the known interatomic distances of silica tetrahedrons and of arrays of tetrahedra.

According to the theory of Tilton (Ref. 5), glass is composed of small clusters of definitely arranged but slightly disordered structural units—vitrons—which in

turn are composed of smaller, more nearly regular units such as the SiO_4 tetrahedra. Vitrons tend to form in a melt and have an approximate noncrystal symmetry (such as fivefold) and are capable of limited continuous growth. Within this vitron structure there are prominent curved or hybrid "planes" in which numerous atoms are located and which produce coherent scattering of X-rays. There is a wide distribution of interplanar distances ranging from approximately 1.6 Å to greater than 6.0 Å. Scattering of X-rays will occur from each of these planes, and the greater the density of planes of a given interplanar distance the more intense will be the X-ray scatter from that set of planes (and at the corresponding Bragg angle). Tilton (Ref. 5) showed theoretically that a prominent set of planes defined by vitrons can exist in silica glass with a statistical d-spacing of 4.2 Å, a distance corresponding to the interplanar distance derived from the observed 2θ value (Table 3) of the pure silica glass diffraction maximum; $2\theta = 21.1^\circ \equiv 4.21 \text{ Å}$.

Therefore, the diffraction maximum from pure silica glass is considered to be the integrated intensity of a very large number of diffraction peaks emanating from a correspondingly large number of semi-ordered structural planes in the glass, which have interplanar spacing with a statistical maximum at intervals of 4.2 Å.

Based on the above concept, the data reported in this study suggest that as pure silica glass is diluted with other constituents so that the SiO_2 content decreases, the average distance between hybrid structural planes in the glass diminishes, more planes with dimensions less than 4.2 Å are created, and the statistical diffraction maxima (by the Bragg relation) shift to higher 2θ angles. The decrease in scattering intensity with decrease in SiO_2 content indicates that the "reflectivity" of the hybrid planes in the glass structure decreases, suggesting that the degree of disorder of planes and of the structure as a whole increases as the silica glass structure incorporates foreign atoms or molecules.

VI. SUMMARY AND APPLICATIONS

It has been shown that the mean 2θ position of glass diffraction maxima have an inverse relation to the SiO_2 content of natural and synthetic silicate glass. It is proposed that such a relationship affords the utilization of standard X-ray diffraction equipment for simple, rapid, inexpensive, and unique determination of total SiO_2 content in silicate materials.

Such semiquantitative determinations can be made by fusing the unknown sample, if it is not already glass, and, with the diffractometer parameters and measuring technique outlined in this Report, determining the mean 2θ position of the diffraction maximum of the glass. From the 2θ value, the SiO_2 concentration can be obtained graphically from curves shown in Fig. 8a and 8b. With diffractometer parameters or measuring techniques other than those used in this study the 2θ values may differ extensively from the values obtained here, and the location and shape of curves in Fig. 8 will be somewhat different.

The accuracy of SiO_2 determinations using the technique described in this Report is at the present time somewhat low, with possible errors of $\pm 1\text{--}4\%$. However, with further investigation and experimentation the accuracy of this technique can be greatly improved.

The glass-maximum technique for semiquantitative silica determinations, besides being relatively simple, does not require measured amounts of sample, in contrast to techniques such as wet chemical or spectrographic analyses, which require accurately weighed portions for correct results. In fact, the silica content of a glass can be determined using the glass-maximum technique even though the glass to be analyzed is diluted by as much as 60 to 70% with crystalline material. Thus in a crystal-glass mixture, such as certain volcanic rocks, the glass fraction can be analyzed without the necessity of separating it from the crystalline fraction.

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